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THE CHEMISTRY OF METALS IN IONOMERS REACTIONS OF
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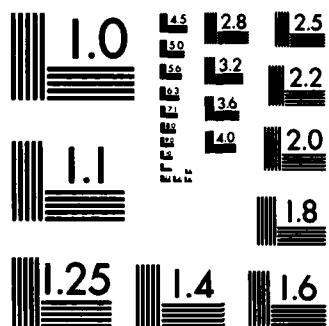
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The Chemistry of Metals in Ionomers: Reactions of
Rhodium-PSSA with CO, H₂ and H₂O

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Abstract

Rhodium(III) ions have been incorporated in ionic domains of sulfonated linear polystyrene (PSSA) to form PSSA-Rh(III) films. The Rh-containing domains can act as isolated chemical reactors, and their chemical interactions have been explored in this work by controlling the exposure of the rhodium sites to CO, H₂ and H₂O under mild conditions. Reaction with CO at low temperature, without either prior reduction by H₂ or complete dehydration of the PSSA-Rh(III) film, resulted in production of a Rh(I)(CO)₂ species. Partial or complete reduction of the films with H₂, proceeded or followed by exposure to CO results in the cis-dicarbonyl and, under various conditions, linear and bridging PSSA-Rh(0) carbonyls, and CO bound to Rh(0) particles. The implications of the results for catalysis are discussed.

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Introduction

Ionomers are polymers that are functionalized with ionic groups attached at various points along the polymeric backbone. These usually are anionic groups, such as carboxylate or sulfonate, and they may be joined directly to the backbone or attached by a short side chain. Ionomeric materials have come under intensive study in recent years because they have important electrochemical and materials applications.

Much of the interest in ionomers is associated with their tendency to form ionic domains in which anionic groups are microphase-separated from the hydrophobic portions of the polymer. Ionic domains are formed in sulfonated linear polystyrene or PSSA, when the degree of sulfonation exceeds a few percent of the available positions along the polystyrene backbone (1, 2). At such ionic group concentrations thermodynamics favors the separation of the ionic components (cations and anionic sites) and the backbone units into hydrophilic regions (the ionic domains) and hydrophobic regions. As a result, the ionic domains are largely surrounded by a medium of low dielectric constant formed by the polymer network, although in some cases the domains may be connected to one another by channels (3). The domains are accessible to cationic species, including transition metal-containing cations, by ion exchange.

Thus, an ionic domain contains anionic sites and metal ions and is a physically surrounded region, typically about 20-100 Å in diameter (3) and can be thought of as a small isolated chemical reactor. If the metal ions in the domains are transition metal ions and can be treated to create active sites, the domains would become isolated chemical reactors containing catalytic centers. The physical structure of the domains contributes to their potential to function as reactors, be-

cause it enables them to confine a reactant molecule in the proximity of an active site and other reactants. Any reactant molecules that diffuse into the domains could be confined for a residence time that would permit the sites and reactants to interact in the domain much as they would if they were surface sites and gaseous reactants from a gas at much higher pressure. The possibility thus exists that reactions can be catalyzed in ionomers under much milder external conditions than would be required otherwise. Moreover, the ionomers have other potential advantages as reactors since the anionic site concentration, and consequently the domain size and other properties, can be controlled. This should permit considerable flexibility in reactor design.

To investigate this possibility we have carried out reactions on metal-exchanged ionomers of several types. One type is PSSA, mentioned above, which has the particular advantage that its members in the H-PSSA form are soluble and can be separated, in principle, from products formed. The other type is exemplified by PFSA, or Nafion, which is not soluble but has the advantage that its backbone is very stable chemically. In this paper we report the formation of Rh-exchanged PSSA and its chemical interactions with CO, H₂ and H₂O. In other papers our work on the reactions of PFSA and PSSA ionomers containing Pd (4), Pt (5), Rh and Ru (6) and other metals will be reported.

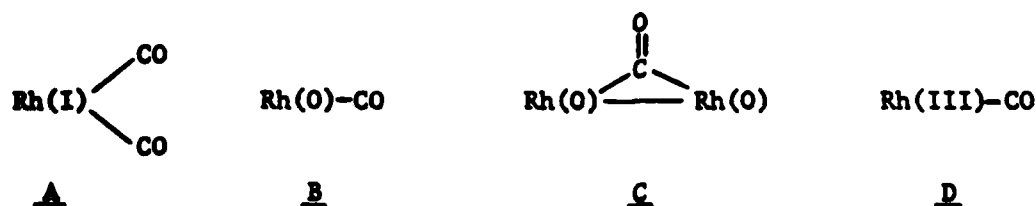
Numerous examples of reactions involving supported Rh, particularly heterogeneous catalysis over supported rhodium surfaces, have been reported. Typically, the catalysts were prepared on oxide supports (e.g. SiO₂, Al₂O₃) by one of two different techniques. In one method the support is impregnated with an aqueous solution of a rhodium salt, and the material is dehydrated, and then reduced at high temperature. This produces a dispersed Rh catalyst with a distribution of metal particle

sizes.

Novel rhodium-containing heterogeneous catalysts have also been prepared by the chemical modification of the ionic sites present in zeolites (7-9) and, in work related to this study, in PFSA ionomer systems (6). In contrast to the surface modified oxides, these catalysts are prepared by ion-exchanging a rhodium cationic species derived from a salt, such as RhCl_3 or $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, dehydrating (or deamminating), and then reducing them in H_2 . Other studies (10-15) have focused on the immobilization of homogeneous catalysts, such as $\text{Rh}_6(\text{CO})_{16}$ onto insoluble supports, including phosphine-functionalized polystyrene in which the support plays the role of a ligand. Using this method, metal cluster interactions can be reduced, thereby maintaining the metal in a state of atomic dispersion.

The reactions of CO on supported rhodium are quite important, and many infrared investigations of the structural features of rhodium carbonyl formed by chemisorption have been carried out. The first study of the infrared spectrum of CO chemisorbed on Al_2O_3 -supported rhodium particles was reported by Yang and Garland (16) and has since been reinvestigated by Yates *et al* (17). Recently, the effects of catalyst loading, oxidation state of rhodium (18), rhodium site distributions (19,20) and the effect of catalyst precursor (21) on the infrared spectra of CO adsorbed on Al_2O_3 -supported rhodium particles have been studied. The results can be compared to those observed for chemisorption of CO on rhodium single crystals (22) and evaporated thin films (23) where the effect of the support is largely removed. While the nature of the underlying support and catalyst preparation may differ, infrared spectral studies suggest the formation of similar rhodium carbonyl species.

At least four different rhodium carbonyl species on supported rhodium surfaces have been identified as those represented by the following:



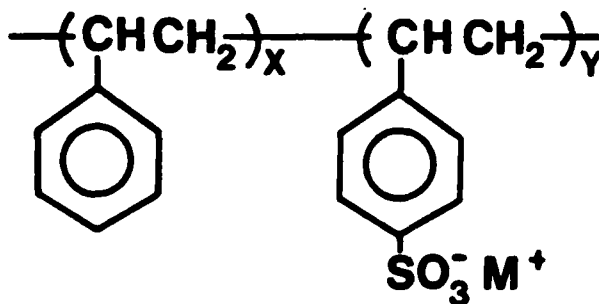
The appearance of two infrared bands of about equal intensity, whose frequencies (ca. 2100 and 2025 cm^{-1}) are independent of the CO coverage and which are affected similarly by various treatments, has been attributed to an isolated cis-rhodium(I) dicarbonyl species, (A), on the basis of comparison to the infrared spectra of compounds of the type $[\text{Rh}(\text{CO})_2\text{X}]_2$ where C = Cl, Br and I. The frequency of the linear rhodium(0) carbonyl species, (B), is thought to be sensitive to the extent of CO coverage and rhodium particle size and structure but usually falls within the range of 2100 to 2000 cm^{-1} . The observation of a band, often actually a broad band structure, in the 1920 to 1780 cm^{-1} region, generally is taken to reflect the presence of a bridging CO species, (C). Species D, or a variant, has been suggested to account for observations in the 2120 to 2180 cm^{-1} region under oxidizing conditions (24).

We report here the infrared spectra due to CO chemisorption at rhodium sites prepared by the chemical modification of PSSA and of reactions of this system with H_2 , H_2O , and O_2 . Although the thermal stability of PSSA is much lower than that of inorganic oxides (zeolites, Al_2O_3 , SiO_2 , etc.) with which these data will be compared, the reactions have been done in this ionomer under such mild conditions and the results are similar. Our results show that rhodium particles can be formed in PSSA and that they and rhodium ions undergo reactions with CO under mild conditions to form rhodium carbonyls analogous to those observed on other supports.

Experimental

The ionomer employed in this study is a sulfonated linear polystyrene, PSSA. Materials of this type have been prepared at various degrees of sulfonation and studied by R.D. Lundberg and coworkers at Exxon Research and Development Company (25).

That used in this work is designated PSSA(16.7) and was kindly provided by Dr. Lundberg. Its chemical composition is represented as follows:



Here, $y/(x+y)$ represents the mole fraction of sulfonate groups. The ionomer used had an average sulfonate composition of 16.7 mole %, and was chosen because the sulfonate groups aggregate at this composition to form ionic clusters dispersed throughout the non-polar matrix (26).

Transparent thin films of PSSA were prepared at ca. 25 μm thickness, which is convenient for study by transmission infrared spectroscopy by dissolving the H^+ form in tetrahydrofuran (THF) and then allowing the solvent to evaporate at 298 K. Rhodium ions were incorporated by an ion-exchange process in which the PSSA films were stirred in water/ethanol solutions (6:1 volume ratio) of rhodium(III) nitrate ($\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ Alfa Products). Completion of ion-exchange was demonstrated by observation of the features in the $\nu(\text{SO}_3^-)$ vibrational region of the infrared spectra (27). The films which became colored bright yellow upon ion-exchange were removed from solution, rinsed with distilled water, and were allowed to air dry prior to loading them in the reactor.

The primary reactor/infrared cell used is shown in Figure 1. It has a pyrex body, with KBr windows affixed with a cyanoacrylate glue, and could be connected conveniently to a vacuum line or gas supply line.

Using this cell, the spectra were taken in situ of films subjected to various treatments. The sample holder, all of whose parts were machined from a PTFE-block, contained PTFE-coated magnets in each end so that the sample-holder could be aligned in the infrared beam using an external magnet. The cell was heated and the temperature controlled by a Variac-regulated heating tape and monitored with a chromel-alumel thermocouple.

The gases used in this work, carbon monoxide (99.99% CO, Matheson Corp.) and hydrogen (99.995% H₂, Airco, Inc.) were purified further by passing the gases through a series of liquid nitrogen traps upon their addition to the reactor.

The infrared spectra in the 3800-400 cm⁻¹ region were recorded at 298 K with a Digilab 15B FT-IR spectrometer. Each trace represents the average of at least 100 scans recorded at 2 cm⁻¹ resolution.

The PSSA-Rh films were treated in the cell described above. The reactions carried out are described in the Results section. In the description the films or species are designated in the form PSSA-Rh(A)B, where A gives the oxidation state assigned and B designates the other chemical constituents.

Results

The infrared spectra of the PSSA-Rh films were recorded first on the material as it was prepared and then after it had been subjected to various dehydration treatments of heating and evacuating the cell. The spectra of the hydrated PSSA-Rh(III) films contain broad bands at ca 3300 cm⁻¹ and 1620 cm⁻¹ due to the $\nu(\text{OH})$ and $\delta(\text{HOH})$ modes of coordinated H₂O, in addition to those of the ionomer. Complete ion exchange was accomplished, so no bands associated with vibrations of SO₃H moieties were found. Since water molecules form strong hydrogen-bonded networks

with the sulfonate groups (28) and are expected to be associated with the highly charged Rh(III) centers, complete dehydration requires heating at elevated temperatures (ca. 443 K) under reduced pressure for times which depend on film thickness. Only partial dehydration of PSSA-Rh(III) films is obtained at $P \approx 10^{-2}$ Torr if the temperature is not raised above 398 K, even for a 7-day period, but it is not necessary to heat these materials above ca 443 K to dehydrate them completely.

In order to investigate the reactions of PSSA-Rh(III) with CO under a variety of conditions, and attempt to use several approaches to obtaining reduced Rh species in the PSSA ionomers, CO was added to partially dehydrated films. The addition of CO at 380 Torr and 298 K to partially dehydrated PSSA-Rh(III) films gave rise to two weak infrared bands in the $\nu(\text{CO})$ region. They appear at 2095 and 2023 cm^{-1} and indicate the formation of a Rh(I)(CO)_2 species. The formation of this species will be discussed in more detail later. But, it is useful to note here that we postulate that PSSA-Rh(III) is reduced to PSSA-Rh(I) in the presence of CO and H_2O by the following reactions:



This postulate is based on an analogy with the reduction of Rh(III) by CO in solution (29). Analogous reactions have been postulated to occur on zeolite-supported rhodium under similar conditions (7).

With further exposure to CO (up to 24 hr) these bands increased slightly in intensity and new ones appeared at 2178 and 2148 cm^{-1} . As also is discussed below, we assign these bands to sigma bound Rh(III)-CO and CO physically adsorbed on PSSA-Rh(III), respectively. When the reaction vessel containing CO as well as the sample was heated for 24 hr

at 368K the spectrum of the film was found to as shown in Figure 2A. The principal features are the 2095 and 2023 cm^{-1} band pair. The bands at 1942 and 1875 cm^{-1} are due to the PSSA-support (30), so for a given PSSA-Rh film, the 1942 cm^{-1} band has a constant absorbance and serves as an internal standard. The spectrum recorded after further heat treatment followed by evacuation of the free gas ($\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$) from the reactor at 298 K is shown in Figure 2B. The 2095 cm^{-1} band appears to be broadened to the high frequency side and suggests the presence of a band at ca 2125 cm^{-1} assigned to a Rh(III)-CO species. At this stage in the reaction sequence the color of the film has changed from yellow to golden brown.

In an attempt to produce Rh(0) carbonyl species in the PSSA ionomer and characterize their reactivities, PSSA-Rh(I)(CO)₂ films were reacted with hydrogen. The spectrum of the PSSA-Rh(I)(CO)₂ film after it was treated with H₂ at 380 Torr and 408 K for 20 hr is shown in Figure 3A. As can be seen by comparison with the spectrum in Figure 2B, the 2094- cm^{-1} band was reduced in intensity by this treatment.

The shape of the broad band at 2020 cm^{-1} in this spectrum makes it appear to arise from at least two types of Rh-CO species. The H₂-treatment also caused the intensity of the 1875 cm^{-1} band, which is due to the formation of bridging carbonyls of zero-valent rhodium, to increase relative to that at 1942 cm^{-1} . Thus, a reduction of Rh(I) to Rh(0) is postulated to have occurred. These results are similar to those of Smith et al (12) who observed bands at 2020 cm^{-1} and 1850 cm^{-1} upon addition of H₂ to Al₂O₃-supported Rh(I)(CO)₂ and are supported by the observation (24) that SiO₂-supported Rh(I)(CO)₂ can be converted readily into Rh(0)-CO sites by the addition of H₂. This also is supported by the observation of a shift in the asymmetric stretching frequency (ν_a) of the -SO₃⁻ group from 1265 to 1227 cm^{-1} which is consistent with the reformation of -SO₃⁻H⁺ sites (28), an important event in the sequence leading to super acid behavior in the presence

of Rh(0) particles.

Further heating at 418 K with H_2 followed by evacuation of the cell at room temperature results in the disappearance of the pair of bands at 2094 and 2023 cm^{-1} and leads to the decrease in frequency of the 2020 cm^{-1} band to 2010 cm^{-1} shown in Figure 3B. In the same spectrum it can be seen that all of the rhodium carbonyl bands have decreased in relative intensity.

Reexposure of partially reduced films to CO at 380 Torr and 298 K for 12 hrs results in a new feature at 2045 cm^{-1} assigned to a linear CO species bound to rhodium particles probably of different size or structure than those which give rise to the 2020 cm^{-1} band. Although we did not directly measure the particle size, we note the striking similarity between the infrared spectrum shown in Figure 4 and that reported by Gates et al (10) for a freshly prepared $Rh_6(CO)_{16}$ phosphine-functionalized polystyrene membrane, which reportedly consisted of rhodium crystallites that were shown to be approximately 40 Å in size by electron microscopy. The spectrum shown in Figure 4 is of a film that had been heated to 408 K for 24 hr, and then evacuated at 298 K. Notice that the 2094 cm^{-1} band and its counterpart at 2023 cm^{-1} , which is superimposed on the low frequency side of the principal band due to Rh(0) at 2045 cm^{-1} , have reappeared. A feature at 1875 cm^{-1} also has reappeared. It is assigned to CO-bridging species, that is, species involving Rh(0) atoms bridged by one or more CO molecules. The films were still translucent at this stage but the color had taken on a blackened appearance.

In order to investigate the nature of CO chemisorption on Rh surfaces in or on PSSA, which qualitatively may be quite similar to those of heterogeneous catalysts, PSSA-Rh(III) films were dehydrated at 438 K and 1×10^{-2} Torr for 24 hr and then treated with H_2 at 380 Torr and

438 K for 24 hr. The infrared spectrum shown in Figure 5A shows no indication of the formation of rhodium hydrides in the 2000 cm^{-1} region. The only apparent change in the infrared spectrum is a shift in the $\nu_{\text{as}}(\text{SO}_3^-)$ band from 1265 cm^{-1} to 1227 cm^{-1} . These observations parallel those discussed earlier and suggest that the reduction of PSSA-Rh(III) occurs with the concomitant formation of Rh(I) and Rh(0) sites. The films have acquired a black color at this stage.

Following reaction of the films with H_2 , chemisorption of CO by these films at 398 K for 48 hr gave rise to the spectrum shown in Figure 5B. The formation of cis-rhodium(I) dicarbonyl (2095 and 2023 cm^{-1}), rhodium(0) carbonyl (2045 cm^{-1}), and the carbonyl bridged Rh(0) species (1875 cm^{-1}) is observed. The absence of $\nu(\text{CO})$ bands above 2100 cm^{-1} supports the deduction that there are no Rh(III) sites present after reduction, but, given the ability of CO and H_2O to effect reduction, it does not prove it. Mild thermal desorption was then carried out by evacuating the reactor at 1×10^{-2} Torr and 373 K. As shown in Figure 6, the 2045 cm^{-1} and 1875 cm^{-1} bands disappear under this treatment while a new band at 1986 cm^{-1} appears. By comparison of this result with those of other studies (22), the band at 1986 cm^{-1} is assigned to a Rh(0)-CO species in which the CO is linearly bound to larger, more stable rhodium particles. Clearly, the bands of the Rh(I)(CO) $_2$ species have been diminished in intensity. The 2023 cm^{-1} component of this vibration apparently is shifted to 2016 cm^{-1} , but that is due to overlap with the 1986-cm^{-1} band.

The results indicate that films of PSSA-"supported" rhodium undergo CO chemisorption under mild reaction conditions. The spectral criteria for carbonyl absorptions as a function of the readily accessible oxidation states of rhodium have been established. The types of PSSA

rhodium carbonyls observed here and their frequencies are listed in Table 1.

The infrared absorption bands of the PSSA support show that no significant changes in it occur during the reactions. Thus, the polymer is assuming a rather passive role during the reactions, although its domain forming ability and the properties of the sulfonate groups are important for ligation, protonation, hydration and charge balance. This is in contrast to the phosphine functionalized polystyrene supported rhodium catalysts (15) in which the oxidation of the phosphine ligands occurs in the presence of the rhodium particles.

Discussion

We have shown that ionomers represent a new class of catalytic supports into which transition metal ions can be incorporated by a simple ion-exchange process. In contrast to the impregnation method of catalyst preparation which often results in the formation of large metallic particles, ionomers offer the additional possibility of forming small transition metal clusters at which new chemistry may be realized under mild reaction conditions. The results of the present study demonstrate that the ionic domains present in PSSA are accessible by cationic ion-exchange and that this process leads to domains that have high local concentrations of metal ions and can be made quite reactive to small gaseous molecules. When even incompletely dehydrated PSSA-Rh(III) films are exposed to CO, Rh(III)-CO and Rh(I)(CO)₂ species are formed through a sequence of reactions including the reduction of Rh(III) to Rh(I), by the water gas shift reaction and reaction of CO with the Rh species present.

The direct reduction of PSSA-Rh(I) (CO)₂ films with H₂ leads to the formation of Rh(O)-CO species and an overall decrease in the amount of Rh(I)(CO)₂. The observation of an infrared band at 2020 cm⁻¹, which is assigned to a linear Rh(O)-CO species, and of a band in the bridging-CO region at 1870 cm⁻¹, suggests the initial formation of small rhodium particles. This is supported by the observation that the films begin to blacken in appearance. This is not unexpected since rhodium atoms, in contrast to the Rh(I) species, are not restricted by chemical bonding to a particular sulfonate site. Furthermore, since the ionic domains provide for an increase in local catalyst concentration, aggregation is favored.


The infrared spectra of PSSA supported rhodium suggest that the reaction products are similar to those formed on other supported rhodium systems. These results suggest that ionomer supported transition metals may be useful catalysts. Catalytic studies involving PSSA and PFSA supported rhodium are in progress.

Acknowledgements

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Table 1

Summary of CO Species Observed on PSSA-Supported Rh

<u>FREQUENCY</u>	<u>ASSIGNMENT</u>
2178	PSSA - σ Rh(III)-CO
2148	Rh(III) CO physical adsorption
2125	Rh(III)-CO
2095	Rh(I) (CO) ₂
2023	
2045	*Rh(O) _x -CO
2020	*Rh(O) _y -CO
1986	*Rh(O) _z -CO
1970	

*x,y,z indicate Rh particles of different sizes or structures.

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FIGURE CAPTIONS

Figure 1: Reactor - IR cell. A: pyrex frame; B: film sample holder machined from PTFE stock; C: PTFE - coated magnets; D: KBr windows sealed to the cell dry; E: vacuum line connection; F: auxilliary gas attachment

Figure 2: A; IR spectrum of a partially dehydrated PSSA-Rh(III) film which was exposed to CO at 380 Torr and 298 K for 24 hr followed by heating at 368 K for 24 hr.

B; IR spectrum of the PSSA-Rh(I)(CO)₂ film heated at 383 K for 48 hr followed by evacuation of the CO from the reactor at 298 K to 22 hr.

Figure 3: A; IR spectrum of the PSSA-Rh(I)(CO)₂ film which was exposed to H₂ at 380 Torr and 408 K for 20 hr.

B; IR spectrum of the same film heated in H₂ at 418 K for 46 hr followed by evacuation of the H₂ from the reactor at 298 K.

Figure 4: IR spectrum of the same film after reexposure to CO at 380 Torr and 298 K for 12 hr.

Figure 5: A; IR spectrum of a freshly prepared PSSA-Rh(III) film which was first dehydrated at 438 K and 1×10^{-2} Torr for 24 hr followed by exposure to H₂ at 380 Torr and 438 K for 24 hr.

B; IR spectrum of the same film which was exposed to CO at 380 Torr and 398 K for 48 hr.

Figure 6: A; Same as Figure 5B

B; IR spectrum of the film after simultaneous evacuation
at 1×10^{-2} Torr of CO and heating at 373 K for 6 hr.

REACTOR-IR CELL

